

SEPARATED FLOW LIQUID CATHOLYTE ALUMINUM
HYDROGEN PEROXIDE SEAWATER SEMI FUEL CELL

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT (1) ERIC G. DOW, (2) SUSAN YAN G. and (3) MARIA G. MEDEIROS, employees of the United States Government, citizens of the United States of America, (4) RUSSELL R. BESSETTE, citizen of the United State of America, and resident of (1) Barrington, County of Bristol, State of Rhode Island, (2) Fairport, County of Monroe, State of New York, (3) Bristol, County of Bristol, State of Rhode Island and (4) Mattapoisett, County of Bristol, Commonwealth of Massachusetts, have invented certain new and useful improvements entitled as set forth above of which the following is a specification.

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23523

PATENT TRADEMARK OFFICE

1 Attorney Docket No. 79530

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3 SEPARATED FLOW LIQUID CATHOLYTE ALUMINUM

4 HYDROGEN PEROXIDE SEAWATER SEMI FUEL CELL

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6 STATEMENT OF GOVERNMENT INTEREST

7 The invention described herein may be manufactured and used
8 by or for the Government of the United States of America for
9 governmental purposes without the payment of any royalties
10 thereon or therefore.

11

12 CROSS REFERENCE TO OTHER PATENT APPLICATIONS

13 Not applicable.

14

15 BACKGROUND OF THE INVENTION

16 (1) Field of the Invention

17 The present invention relates to a liquid catholyte
18 aluminum-hydrogen peroxide seawater semi fuel cell which has
19 particular utility as an energy source for underwater vehicles.

20 (2) Description of the Prior Art

21 Primary batteries employing aqueous electrolytes have been
22 under development since the 1940s. U.S. Patent Nos. 4,296,184
23 to Stachurski, 4,352,864 to Struthers, 4,485,154 to Remick et

1 al, 4,492,741 to Struthers, and 5,496,659 to Zito show some of
2 the electrochemical power cells that have been developed.

3 The '184 patent to Stachurski illustrates an
4 electrochemical cell which has at least two compartments
5 separated by a semi-permeable membrane. The compartments
6 contain first and second solvents, electrolyte and electrode.
7 The first compartment is divided by a membrane which behaves as
8 a bipolar electrode during the passage of electric current.

9 The '864 patent to Struthers illustrates a fuel cell which
10 has a metal anode immersed in a base electrolyte solution and
11 connected with an electric circuit, a cathode comprising an acid
12 solution, a carbon catalyst and electron distributor plate in
13 that solution and connected with an electron supply and a
14 wettable impermeable membrane and disposed between the
15 electrolyte and cathode solution and establishing an acid-base
16 reaction interface where hydroxide ions are generated for
17 conduction through the electrolyte to the anode.

18 The '154 patent to Remick et al. illustrates an
19 electrically rechargeable anionically active reduction-oxidation
20 electric storage-supply system and process. The system and
21 process use a sodium or potassium sulfide-polysulfide anolyte
22 reaction and an iodide-polyiodide, chloride-chlorine, or
23 bromide-bromine species catholyte reaction. The catholyte and
24 anolyte are separated by an ion selective membrane permeable to

1 positive sodium and potassium ions and substantially impermeable
2 to negative bromide, chloride, iodide, sulfide and polysulfide
3 ions.

4 The '741 patent to Struthers illustrates a primary fuel
5 cell including an elongate case defining a central ion exchange
6 compartment with opposite ends and containing a liquid ionolyte.
7 The case also defines an anode section at one end of the case
8 and including a gas compartment containing boron monoxide gas
9 fuel, a liquid compartment between the gas compartment and the
10 ion exchange compartment and containing a liquid anolyte. The
11 ionolyte and anolyte are separated by a cationic membrane. The
12 gas and liquid compartments are separated by an anode plate
13 including an electron collector part, a catalyst material
14 carried by the part and a gas permeable hydrophobic membrane
15 between the boron monoxide gas and the catalyst material.

16 The '659 patent to Zito illustrates an electrochemical
17 apparatus having at least one cell. Each cell has a positive
18 electrode and a negative electrode with a dual membrane in each
19 cell dividing it into positive chambers for posilyte and anolyte
20 solutions which are recirculated through separate pumps and
21 storage tanks and back to the chambers. The dual membranes in
22 each cell provide a third chamber between the positive chamber
23 and the negative chamber through which an idler electrolyte is
24 circulated.

1 Emphasis has been placed on aluminum and magnesium anodes
2 due to their high faradic capacity, low atomic weight and high
3 standard potentials. Of particular interest is their
4 application to undersea vehicles due to the availability of
5 seawater to act as an electrolyte or electrolyte solution, thus
6 further enhancing their effectiveness as an energy source on a
7 systems basis.

8 A useful electrochemical energy source must permit high
9 voltages, have a large storage capacity, operate safely, and
10 reliably deliver the stored energy over extended discharge
11 times. Therefore, the energy source must achieve a reasonably
12 high cell potential, have a high Faradaic capacity, and have a
13 high energy density at low current densities. Additionally, the
14 energy source must be relatively inexpensive, environmentally,
15 and SSN friendly, safe, capable of a long shelf life, and not
16 prone to spontaneous chemical or electrochemical discharge.

17 High energy density Al-Aqueous primary batteries and semi-
18 fuel cells for high current density ($>500 \text{ mA/cm}^2$) applications
19 have been developed. These include aluminum-silver oxide and
20 aluminum-hydrogen peroxide semi-fuel cells. U.S. Patent No.
21 5,445,905 to Marsh et al. illustrates one such battery. In the
22 Marsh et al. patent, a dual flow aluminum hydrogen peroxide
23 battery is provided comprising an aqueous hydrogen peroxide
24 catholyte, an aqueous anolyte, a porous solid electrocatalyst

1 capable of reducing the hydrogen peroxide and separating the
2 anolyte from the catholyte, and an aluminum anode positioned
3 within the anolyte. The separation of the catholyte and anolyte
4 chambers helps prevent hydrogen peroxide poisoning of the
5 aluminum anode.

6 Despite these systems, there remains a need for a system
7 with still better performance, particularly one in which the
8 chemical reaction of the solution phase catholyte with the
9 aluminum anode is eliminated.

10 SUMMARY OF THE INVENTION

11 Accordingly, it is an object of the present invention to
12 provide a semi-fuel cell which has improved performance.

13 It is a further object of the present invention to provide
14 a semi-fuel cell as above which has improved electrochemical
15 efficiency and which can be used as a seawater energy source.

16 It is still a further object of the present invention to
17 provide an improved method for operating a semi-fuel cell.

18 It is yet another object of the present invention to
19 provide an improved cathode for use in a semi-fuel cell.

20 The foregoing objects are attained by the semi-fuel cell,
21 the method, and the cathode of the present invention.

22 In accordance with the present invention, a semi-fuel cell
23 broadly comprises a housing, an anode and a porous cathode in
24

1 the housing, an aqueous catholyte stream flowing within the
2 housing, an aqueous anolyte stream flowing in the housing and
3 separated from the catholyte stream, and means for preventing
4 migration of the catholyte through the porous cathode and into
5 the anolyte stream. In a preferred embodiment of the present
6 invention, the anolyte stream comprises a stream of
7 NaOH/seawater electrolyte, the catholyte comprises an aqueous
8 hydrogen peroxide solution, and the preventing means comprises a
9 membrane attached to or impregnated into the porous cathode,
10 which membrane allows passage of OH^- ions through the membrane
11 while inhibiting the flow of hydrogen peroxide through the
12 membrane.

13 In accordance with another aspect of the present invention,
14 a method for operating a semi-fuel cell broadly comprises the
15 steps of: providing a housing having at least one anode and at
16 least one porous cathode; flowing a catholyte stream into
17 contact with said at least one porous cathode through at least
18 one catholyte channel; flowing an anolyte stream into contact
19 with at least one anode through at least one anolyte channel;
20 and preventing contact between each respective anolyte stream
21 and each respective catholyte stream.

22 Other details of the semi-fuel cell of the present
23 invention, as well as other advantages and objects attendant
24 thereto, are set forth in the following detailed description and

1 the accompanying drawings wherein like reference numerals depict
2 like elements.

4 BRIEF DESCRIPTION OF THE DRAWINGS

5 FIG. 1 is a schematic representation of a typical semi-fuel
6 cell stack with a bi-polar cell stack configuration;

7 FIG. 2 is a schematic representation of the reactions which
8 occur in the cell of FIG. 1; and

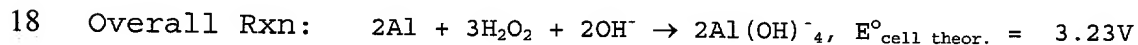
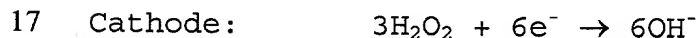
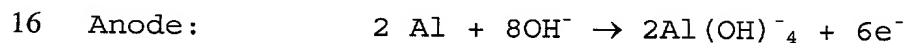
9 FIG. 3 is a schematic representation of a semi-fuel cell
10 stack in accordance with the present invention.

12 DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

13 FIG. 1 illustrates a typical solution phase catholyte semi-
14 fuel cell stack 10. Solution phase means that the cathodic
15 species is in solution with the flowing aqueous electrolyte
16 within the cartridge cell stack. The semi-fuel cell stack 10
17 has an anode end plate 12, a cathode end plate 14, and a
18 plurality of intermediate bipolar electrodes 16. The bipolar
19 electrodes 16 are each metallic aluminum or magnesium anodes
20 plated on one side with an inert conductive substrate such as
21 nickel, copper or carbon catalyzed with palladium, iridium, or
22 silver. This configuration results in a planar bipolar stack of
23 cells 18 electrically connected in series.

1 Each cell stack 18 is hydraulically fed in parallel via an
2 inlet conduit 20 with seawater and a low-concentration, 4 wt%
3 sodium hydroxide aqueous electrolyte. The catholyte, consisting
4 of a hydrogen peroxide solution, is carried separately and
5 injected directly into the electrolyte and seawater mixture
6 upstream of the cell gap at the required concentration, as
7 determined by the system power load. An outlet conduit 22 is
8 provided to remove spent electrolyte and spent catholyte.

9 Electrochemical reduction of the cathodic species, or
10 catholyte, occurs on the electrocatalyst surface of the
11 electrodes 16, receiving electrons from the anode oxidation
12 reaction, which is depicted in FIG. 2. In a system such as
13 this, the half cell and overall cell reactions can be written as
14 follows:
15



19 The problem with this type of system is that the catholyte,
20 in this case hydrogen peroxide, is allowed to come into direct
21 contact with the aluminum anode, resulting in a parasitic direct
22 chemical reaction which does not produce electron transfer and
23 only consumes active energetic materials, thus reducing the
24 overall energy yield of the system. In most cases, this

1 parasitic reaction will consume over 50% of the available
2 energetic materials.

3 FIG. 3 illustrates an aluminum-hydrogen peroxide separated
4 semi-fuel cell stack 30 in accordance with the present
5 invention. The cell 30 eliminates the aforementioned parasitic
6 reaction by not having the hydrogen peroxide catholyte mixed
7 with the seawater and sodium hydroxide electrolyte. In fact,
8 the two are maintained separate.

9 The cell stack 30 has a housing 32 which may be formed from
10 any suitable material known in the art. Within the housing 32
11 are positioned a one or more anodes 34 and one or more cathodes
12 36. Each anode 34 is preferably formed from an aluminum
13 containing material such as an aluminum alloy. Each cathode or
14 positive electrode 36 is formed from a porous, electrically
15 conductive material which has been catalyzed with at least one
16 of palladium and iridium to effect improved electrochemical
17 reduction of the catholyte. In a preferred embodiment, each
18 cathode 36 is formed from a carbon fiber matrix material which
19 has been catalyzed with palladium and iridium.

20 Attached to a first surface 37 of each anode 34 is a member
21 38 formed from an electrically non-conductive material such as a
22 polypropylene material. The member 38 is shaped to form a
23 number of flow channels 40 for the catholyte solution. The

1 member 38 may be attached to the surface 37 of the anode 34
2 using any suitable means known in the art such as an adhesive.

3 Attached to a second surface 42 of each anode 34 is a
4 plurality of separators 44. The separators 44 are also
5 preferably formed from an electrically non-conductive material
6 such as a polypropylene material and also may be attached to the
7 surface 42 using any suitable means known in the art.

8 The cell stack 30 further has inlet means (not shown) for
9 supplying the catholyte such as an aqueous hydrogen peroxide
10 solution to the flow channels 40. If desired, the cell stack 30
11 can have an outlet means (not shown) for exhausting spent
12 catholyte.

13 In accordance with the present invention, each cathode 36
14 is provided with means 46 for preventing migration of the
15 catholyte through the porous cathode structure. The migration
16 prevention means 46 preferably comprises a material or membrane
17 which allows OH^- ions which are created during the reduction of
18 the catholyte to pass through itself while inhibiting the
19 passage of hydrogen peroxide through the material or membrane
20 46. The material or membrane may be attached to a surface 47 of
21 the respective cathode 36 so as to cover the surface 47.
22 Alternatively, the material or membrane may be impregnated into
23 the respective cathode 36. When a membrane is used for the

1 migration preventing means 46, the membrane may be a micro-
2 porous membrane or an anion selective membrane.

3 As can be seen from FIG. 3, the cell 30 has one or more
4 flow channels 48 for the anolyte, which is preferably a
5 NaOH/seawater electrolyte. The flow channels 48 are located
6 between the anode surface 42 and a surface of the cathode 36
7 containing the migration preventing means 46. As can be seen
8 from this description, the anolyte flowing through the channels
9 48 never comes into contact with the catholyte. The cell stack
10 30 may be provided with inlet means (not shown) for supplying
11 anolyte to each of the flow channels 48 and outlet means (not
12 shown) for exhausting spent anolyte from each of the flow
13 channels 48. Further, the hydrogen peroxide catholyte is
14 introduced into the semi-fuel cell 30 on the side of the cathode
15 or positive electrode 36 away from the anode 34.

16 As mentioned before, the migration preventing means 46
17 allows ions which are created during the reduction of the
18 hydrogen peroxide catholyte to travel into the NaOH/seawater
19 electrolyte to complete the charge balance during the
20 electrochemical reaction.

21 The operation of semi-fuel cell stack 30 requires the
22 separate metering of the liquid hydrogen peroxide catholyte so
23 that the catholyte is not mixed with any seawater or electrolyte

1 as it enters or exits the cell stack 30. If desired, the
2 catholyte flow may be dead ended within the cell stack 30.

3 In a preferred embodiment of the present invention, the
4 seawater electrolyte is mixed with sodium hydroxide, injected
5 into the flow channels 48 and passed through the cell stack 30.
6 This is desirable to carry heat and $\text{Al}(\text{OH})_4^-$ reaction product out
7 of the cell stack 30.

8 The concentration of the hydrogen peroxide metered into the
9 cell stack 30 can be at concentrations as high as about 70% or
10 as low as about 0.001%. The static hydraulic pressure of the
11 hydrogen peroxide liquid channel(s) 40 preferably is greater
12 than the sodium hydroxide/seawater pressure. This difference in
13 pressure is a function of the cathode and/or membrane porosity.

14 Introduction of a separate flow channel for the pure
15 hydrogen peroxide catholyte eliminates solution phase mixing.
16 Prior art cells had separated flow but used a mixed flow of
17 hydrogen peroxide and seawater and sodium hydroxide, requiring
18 greater volume flow capacity, thus yielding lower energy
19 density. Incorporation of an anion-selective or micro-porous
20 membrane onto the surface or within the surface of each cathode
21 36 is most advantageous. The membrane allows OH^- ions to pass
22 through it, and inhibits the transfer through it of hydrogen
23 peroxide liquid. Prior art cells had mixed hydrogen peroxide
24 with sodium hydroxide, which results in the de-protonation of

1 the hydrogen peroxide into HO_2^- ions. The anion selective
2 membrane would be ineffective under these prior art
3 circumstances.

4 One of the advantages to the semi-fuel cell of the present
5 invention is improved electrochemical efficiency by upwards of
6 75%. This is achieved by reducing and substantially eliminating
7 the chemical reaction which occurs in solution phase semi-fuel
8 cells between the catholyte and the anode.

9 The half cell and overall cell reactions for the cell 30 of
10 the present invention can be written as follows:

11
12 Anode: $2\text{Al} + 8\text{OH}^- \rightarrow 2\text{Al}(\text{OH})_4^- + 6\text{e}^-$

13 Cathode: $3\text{H}_2\text{O}_2 + 6\text{e}^- \rightarrow 6\text{OH}^-$

14 Overall Rxn: $2\text{Al} + 3\text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow 2\text{Al}(\text{OH})_4^-$.

15 The semi-fuel cell configuration of the present invention
16 could be used for other liquid phase catholyte semi-fuel cells
17 with aluminum alloy anodes and other liquid catholytes such as
18 sodium hypochlorite. In other systems, the particular membrane
19 used for the migration preventing means 46 may be chosen on the
20 basis of the particular anions or cations which are to be
21 transferred.

22 The semi-fuel cell stack 30 of the present invention can be
23 used as energy systems such as those required for undersea

1 vehicle applications requiring high energy storage such as
2 torpedo propulsion and unmanned underwater vehicle applications.

3 It is apparent that there has been provided in accordance
4 with the present invention a separated flow liquid catholyte
5 aluminum hydrogen peroxide seawater semi- fuel cell which fully
6 satisfies the objects, means, and advantages set forth
7 hereinbefore. While the present invention has been described in
8 the context of specific embodiments thereof, other alternatives,
9 modifications, and variations will become apparent to those
10 skilled in the art having read the foregoing description.

11 Therefore, it is intended to embrace those alternatives,
12 modifications, and variations as fall within the broad scope of
13 the appended claims.